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**Partial replacement of fossil fuels in a cement plant:
Assessment of human health risks by metals and PCDD/Fs**

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ABSTRACT

In 2009, a cement plant located in Alcanar (South Catalonia, Spain) started co-processing a special kind of refuse-derived fuel (RDF) called ENERFUEL™. In April 2014 and 2017, 5 and 8 years after RDF co-processing, the levels of metals and PCDD/Fs were measured in samples of soils, herbage and air collected in the vicinity of the facility. The comparison of the current concentrations with those obtained in a baseline study (2008), when fossil fuels were used solely, has shown that the environmental levels of metals and PCDD/Fs were not significantly modified. The levels of metals and PCDD/Fs in soil, vegetation and air of Alcanar are in the low part of the ranges found around other cement plants in Catalonia. Non-carcinogenic risks due to exposure to metals and PCDD/Fs were lower than the safety value (HQ<1). In turn, carcinogenic risks were below the national 10^{-5} threshold. The present results corroborate that, from an environmental point of view, the use of wastes as alternative fuels (AF) in a cement plant, which is operating with suitable technical conditions, is a good option for waste management. It contributes towards overcoming challenges such as climate change and fossil fuel depletion, while utilizing principles of circular economy.

Key words: Cement plant, PCDD/Fs, metals, monitoring, human health risks

1. Introduction

Cement production has increased around the world as a consequence of the grown of population and urbanization ratio (Shen et al., 2017). It is well known that the manufacture of cement may have important environmental consequences since it requires large quantities of raw materials, mainly limestone, as well as of energy, which has been traditionally obtained from fossil fuels such as coal, petroleum coke (pet-coke) and natural gas. Cement industry has been identified as one of the main emitters of particles, NO_x, SO_x and CO₂, being the second main emitter of CO₂, just after power industry (Sánchez-Soberon et al., 2015; Schuhmacher et al., 2004; Shen et al., 2017). Hence, the production of cement has a relevant role in the global warming and climate change that has induced the introduction of legislations and incentives to regulate and reduce the CO₂ emissions.

The traditional linear extract-produce-use-dump material and energy flow model implemented so far in the modern economic system has been proved unsustainable at long term (Korhonen et al., 2018). In contrast, the circular economy provides the economic system an alternative that fosters to reduce negative environmental impacts and stimulate new business opportunities. In this line, most materials (including biomass and waste-derived fuels such as tires, sewage sludge (SS) and municipal solid wastes (MSW)) contain some potential energies that can be utilized by cement industries in order to meet the requirements of the thermal energy, while respecting the waste hierarchy established by the Waste Framework Directive (2008/98EC) (Malinauskaite et al., 2017). Therefore, the use of those materials as a source of energy in cement plants contributes towards overcoming challenges such as climate change, waste management and fossil fuel depletion, while utilizing principles of circular economy (ECOFYS, 2016; Malinauskaite et al., 2017). On the other hand, unsuitable technical conditions in co-processing cement plants may lead to the emission of some of the most hazardous pollutants, such as heavy metals and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Mari et al., 2009). Consequently, a number of recent studies have been aimed at evaluating the environmental impact of co-processing cement plants (Georgiopoulou and Lyberatos, 2017; Mari et al., 2017; Richards and Agranovski, 2017; Rovira et al., 2014, 2015, 2016).

Since the 1960s, a cement plant with a production capacity of around 2.3 million tons/year is operating in the village of Alcanar (South Catalonia, Spain). In recent years, this facility has made an important effort to improve in terms of sustainability and product quality. One of the main changes at the productive level has been the partial replacement of fossil by alternative fuel (AF). In July 2009, the plant started using a special kind of refuse-derived fuel (RDF) called ENERFUEL™. This RDF is obtained from the “rest” fraction of the municipal solid waste, being formed by plastics (35%), paper and carton (30%), wood (20%) and textiles (15%), having a calorific value around 3750 kcal/kg. In order to assess the potential impact of the co-incineration in the surroundings of the plant, an environmental campaign was designed. Baseline levels of metals and PCDD/Fs were determined in soils, herbage and air around the plant before (October 2008) and after (October 2009) the partial replacement of traditional fossil by alternative fuel. No significant increases in the environmental levels of metals and PCDD/Fs in the surroundings of the facility were then detected (Rovira et al., 2010). Notwithstanding, considering the rather short time elapsed between those monitoring surveys, we estimated necessary to ensure that long- term changes were not occurring in the immission levels of metals and PCDD/Fs.

The present study was aimed at determining the environmental levels of metals and PCDD/Fs -around the cement plant of Alcanar- in two new monitoring campaigns conducted in April 2014 and 2017, 5 and 8 years after RDF co-processing, respectively. The temporal trends, as well as the human health risks for the population living in the neighbourhood were also assessed.

2. Materials and methods

2.1. Sampling

In April 2014 and April 2017, samples of soil, vegetation and air were collected in five sampling points located between 500 m and 7.5 km from the cement plant of Alcanar (Fig. 1). The sampling sites were the same than those in our previous campaigns (2008 and 2009) (Rovira et al., 2010), with the only exception of two points of vegetation and soil, which had been included in the previous surveys, which were

now discarded (Solimar and Ulldecona Urbanization). In contrast, in the current studies, an additional air sample was collected in a point (N° 5) located in the city of Sant Carles de la Ràpita. Sampling points were chosen according to the results of a previous modelling study, as well as the specific location of populated nuclei, including especially sensitive population (children, old people, etc).

No precipitation was recorded during the five days prior/or during the sampling. Prevalent winds in the area are those blowing from Northwest and South. Details on sampling and analytical methodology have been previously described (Rovira et al., 2010). Briefly, air samples were collected by using 2 high-volume active samplers (Tisch Environmental, Cleves, OH, USA), TE-1000-PUF and TE-6070-DV, for determining PCDD/Fs and heavy metals (adsorbed to PM₁₀), respectively. Sampling volumes were within the range 522–605 m³ for PCDD/Fs, and 1567–1720 m³ for particulate matter. For organic pollutants, the particulate and gas phases were separately collected with a quartz fibre filter (QFF) and polyurethane foam (PUF), respectively. In turn, a QFF was used for the sampling of PM₁₀. Soil samples (500 g approximately), which consisted on four subsamples collected within an area of 25 m², were taken from the upper 5 cm of ground, kept in polyethylene bags, and immediately transported to the laboratory. Subsequently, they were dried at room temperature for 2 days and sieved through an aluminum 2 mm mesh screen. Finally, around 150 g of vegetation samples (*Piptatherum* L.) were obtained by cutting the plants at 5 cm above ground, and dried at room temperature. Afterwards, green leaves were crushed with a grinder, and packed in aluminium double foils. Samples were finally stored at –20 °C until analysis.

2.2. Analytical methods

2.2.1. Metals

The pre-treatment of soil, vegetation and air samples was recently described by Rovira et al. (2010). Briefly, 0.5 g of soil/ vegetation sample was treated with 5 ml of HNO₃ (65% Suprapur, E. Merck, Darmstadt, Germany) in a Milestone Start D Microwave Digestion System for 10 min until reaching 165 °C, and kept at this temperature for 20 min. In turn, QFFs were treated with a mixture of 2 ml of HNO₃

(65% Suprapur, E. Merck) and 3 ml of HF (37.5%, Panreac SA, Castellar del Vallès, Barcelona, Spain) in hermetic Teflon bombs for 8 h at room temperature, and 8 h at 80 °C. After cooling, extracts were filtered and made up to 25 ml with ultrapure water. The contents of arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), thallium (Tl), vanadium (V) and zinc (Zn) were determined (in the three environmental monitors) by means of inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000). Blank and control samples, as well as reference materials (Soil, Loamy clay, Resource Technology Corporation US, CRM 052, for soil and air, and Spinach leaves, US NIST, SRM 1570a, for vegetation) were used to check the accuracy of the instrumental methods. The recovery percentages of the reference materials were: 79–108%, 91–115% and 90–113%, for soil, vegetation and air, respectively.

2.2.2. PCDD/Fs

The analysis of PCDD/Fs in soil and vegetation samples was done by High Resolution Gas Chromatography coupled to High Resolution Mass Spectrometry (HRGC/HRMS), in combination with the isotope dilution technique. It was based on the US EPA method 1613. The concentrations of PCDD/Fs in air were determined by HRGC/HRMS, following the German VDI 3499 method. Appropriate labelled extraction standards ($^{13}\text{C}_{12}$ -PCDD/Fs substituted congeners) were added in order to control the whole sample preparation process and to evaluate potential losses. An Accelerated Solvent Extraction (ASE) was carried out by using toluene. The extract was then concentrated and divided into separate parts for the determination of the target compounds. The clean-up procedure was carried out by using adsorption chromatography on a mixed silica column and adsorption/ fractionation on alumina. The final obtained PCDD/F-extracts were injected and analyzed separately on an Agilent 6890 Capillary Gas Chromatograph equipped with a DB5-MS capillary column and coupled to a Waters Autospec Ultima High Resolution Mass Spectrometer, with selected ion recording at resolution of 10,000. Recovery percentages were 75–110%, 58–90% and 72–114% for soil, vegetation and air samples, respectively.

3. Results and discussion

3.1. Environmental Impact: Immission levels of metals and PCDD/Fs

Tables 1, 2 and 3 show the concentrations of metals and PCDD/Fs in soil, herbage and air samples collected around the cement plant of Alcanar in 2014 and 2017, 5 and 8 years after RDF co-processing, respectively. The levels found in the baseline survey (2008) are also shown. To have comparable values, we recalculated the mean levels of metals and PCDD/Fs in soils and herbage from the baseline survey (2008), taking into account the same 5 sampling sites considered in the 2014 and 2017 campaigns, instead of the 7 contemplated initially Rovira et al. (2010).

In soils, no significant differences were found between the concentrations of metals in the current and the baseline campaigns (Table 1). In all surveys, the levels of metals in soils under the potential influence of the cement plant were below the reference levels established for human health protection by the Waste Agency of Catalonia (ARC, 2009). Regarding PCDD/Fs in soils, with the exception of 1,2,3,7,8-PeCDF, whose levels decreased in 2017 ($p < 0.05$), no significant differences were noted between the concentrations found before and after partial fuel replacement, being the total concentrations 0.57, 0.72 and 0.36 ng WHO-TEQ/kg, in 2008, 2014 and 2017, respectively. Currently, there is no legal framework for PCDD/Fs in soils, neither at European, nor at Spanish level. However, guidance levels have been regulated in different countries. For example, in Canada, a soil quality standard for agricultural, residential, and commercial land uses has been established at 4 ng TEQ/kg (CCME, 2002). In turn, in Germany, a target value of 5 ng I-TEQ/kg has been set for preventive reasons in agricultural soils (FEA, 1993). The concentrations of PCDD/Fs in soils of Alcanar were well below those limits in all cases.

In herbage, important fluctuations were noted between periods, with significant decreases for Co, Cr, Cu, Mn and Ni ($p < 0.05$) between 2008 and 2017, but with significant increases for Tl during the same period ($p < 0.05$). No significant differences were observed for individual or total PCDD/Fs between 2008 and 2017, or between 2014 and 2017.

In air, a general decrease in the concentrations of metals was observed between 2014 and 2017, after the previous increase noted in the 2014 campaign. However, the decrease in the period 2014-2017 was significant only for Cr, Ni, Sb and V ($p < 0.05$). No differences were noted between the current (2017) and baseline (2008) metal levels in air ($p > 0.05$). The current European legislation restricts the concentrations of Pb (1999/30/EC) and Ni, As and Cd (2004/ 107/EC), with mean annual limits of 500, 20, 5 and 6 ng/m³, for Pb, Ni, Cd and As, respectively. Although the current concentrations do not correspond to mean annual values, they were far below those reference limits in all cases. No significant differences were noted in the total air PCDD/Fs concentrations before and after co-incineration. However, for some individual congeners, namely 1,2,3,4,6,7,8-HpCDD, 2,3,4,7,8-PeCDF, 1,2,3,7,8,9-HxCDF and 2,3,4,6,7,8-HxCDF, decreases were noted in the period 2008-2017 ($p < 0.05$).

In general terms, the levels of metals and PCDD/Fs in soil, vegetation and air found in Alcanar were in the low part of the range found around other cement plants of Catalonia (NE Spain) (Mari et al., 2017; Rovira et al., 2011a,b,c, 2014, 2015, 2016). The global analysis of the temporal trends of those pollutants in the environmental matrices used as indicators of long-term (soil), short term (herbage), and present (air) emissions, showed that the environmental levels had not been significantly altered after 8 years of co-processing RFD.

The most common alternative fuels used by the cement industry include waste oils, solvents, plastics, textiles, rubber and tires, sewage sludge, agricultural waste, animal meal and fats (Cembureau, 1999; Rahman et al., 2013; Tsakiridis et al., 2017). A number of recent studies have been conducted in order to evaluate the impact of co-incinerating different types of AF in terms of environmental impact, quality of the product and economical costs. Bourtsalas et al. (2018) evaluated the use of an AF composed by non-recycled plastics and paper as AF, by means of Life Cycle Assessment (LCA) in a plant located in San Antonio (Texas, USA). It was concluded that the use of the AF had no adverse effect on the stack emissions, or on the quality of cement produced while leading to environmental and economic benefits. In turn, Richards and Agranovski (2017) examined the effect of different rates of substitution of diverse AFs (waste oil, solvents, chipped wood, refuge waste, carbon dust, shredded tires and black sand) on the emissions of health-critical dl-PCBs (dioxin-like polychlorinated biphenyls) congeners in cement plants of Australia. Their findings

showed that waste co-incineration during cement operations reduced health-critical congeners of dioxins and dl-PCBs, but providing the necessary energy and calcination needs. On the other hand, Fyffe et al. (2016) assessed the energetic and environmental benefits of converting non-recycled post-consumer plastics and fibre into an AF for use in a cement kiln. They performed an LCA study based on the data generated in an experimental test burn. It was concluded that SO₂ emissions were reduced and those of NO_x increased, while the estimated changes in emissions of particulate matter, mercury, hydrogen chloride, and total-hydrocarbons were all less than $\pm 2.2\%$. Also recently, Georgiopoulou and Lyberatos (2017) used LCA methodology to compare seven scenarios, including the use of diverse AFs namely RDF, TDF (Tire derived fuel) and BS (Biological Sludge), as well as mixtures of them in partial replacement of conventional fuels such as coal and pet coke. It was found that the most environmentally friendly prospect was the scenario based on RDF, the same evaluated in our current study, while the less preferable scenario was that based on BS.

3.2. Human health risks

The circular economy is at the top of the EU agenda and the recovery of energy from wastes supports the EU objectives of the circular economy action plan (Malinauskaite et al., 2017). In relation to this line, the EU recommends various best available technologies, being co-incineration in cement kilns among them. However, one of the challenges of the use of AFs in cement kilns is to face the frequent local protests (known as Not In My Backyard syndrome) in populated areas. As one of the most significant factors influencing the Not In My Backyard syndrome is the risk perception, it is essential to conduct an appropriate risk evaluation, and subsequent risk communication. With respect to it, studies evaluating the potential risks of this kind of facilities and their dissemination are basic. In the present study, we used the environmental levels of metals and PCDD/Fs measured in April 2014 and 2017 to assess human health risks 5 and 8 years after RDF co-processing. The current results were compared with those obtained in the baseline survey (2008). The human health risk assessment methodology was that described by Rovira et al. (2010). All the equations (Eqs.1 to 8) and parameters (Table 1) used for exposure assessment and risk characterization are shown in the Supplementary Materials.

The exposure to metals and PCDD/Fs for the population living in the vicinity of the cement plant is summarized in Table 4. In general, for all elements and periods, soil ingestion was the main pathway of exposure (with a percentage generally higher than 90%), followed by dermal contact. For Cu and Sb, ingestion was the main exposure pathway, but with a lower rate (between 70% and 80% for Cu, and 58 and 41% for Sb) followed by inhalation (with rates between 20% and 28% for Cu, and 41 and 60% for Sb). On the other hand, As dermal contact was slightly higher than oral ingestion, with mean percentages of 51 and 48%, respectively. For PCDD/Fs, total environmental exposures were estimated to be 3.41×10^{-6} , 4.46×10^{-6} and 3.41×10^{-6} ng WHO-TEQ/kg·day in 2008, 2014 and 2017, respectively. The main exposure pathway was inhalation, with rates of 50%, 48%, and 38% in 2017, 2014 and 2008, respectively. Soil ingestion and dermal contact showed similar contributions. The non-carcinogenic risks for metals and PCDD/Fs, represented by the hazard quotient (HQ), in the three evaluated periods are depicted in Figure 2. The HQ is calculated as the ratio between the predicted exposure and the corresponding Reference Dose. In all cases, the HQs were lower than the safety value, which is defined as the unity, being the values before (2008) and after (2014 and 2017) the fuel replacement, very similar. Ingestion showed the highest HQ for Co, Hg, Pb, Sb, Tl and V. In turn, dermal contact presented the highest HQ for As and Cr, with inhalation for Mn and Ni. For Cd and Cu, the highest HQ pathway varied among periods. The HQ for PCDD/Fs were $3.10 \cdot 10^{-3}$, $3.48 \cdot 10^{-3}$ and $1.74 \cdot 10^{-3}$ in 2008, 2014 and 2017, respectively. Again all were considerably lower than the safe threshold ($HQ < 1$). Results of the estimated carcinogenic risks of metals and PCDD/Fs are shown in Figure 3. Cancer risk was estimated only for those elements for which slope factors have been established by the USEPA (2017). It includes As and PCDD/Fs ingestion, dermal absorption, and inhalation, as well as Cd, Co, Cr, and Ni inhalation. Although in 2008 ingestion and dermal contact risks for As were slightly higher than 10^{-5} , the acceptable excess of cancer risk (1 out of 100,000 for lifetime exposed individuals), in 2014 and 2017 all the carcinogenic risks were below that acceptable limit established by the Spanish MMA (2007). The overall non-carcinogenic and carcinogenic risks were comparable to those obtained in the baseline study, when petroleum coke was being used as the only fuel. It indicates that the use of RDF as an alternative option to fossil fuels does not mean any additional health risk for the population living in the vicinity of the cement plant.

4. Conclusions

In order to evaluate the potential long term impact of the use of RDF as AF in the cement plant of Alcanar, in 2014 and 2017, 5 and 8 years after RDF co-processing, we measured the concentrations of metals and PCDD/Fs in soils, herbage and air around the plant. These concentrations were compared with those obtained in the baseline survey performed in 2008, when only traditional fossil fuel was being used. In general terms, no significant differences were noted in none of the above environmental matrices used as indicators of long-term (soil), short term (herbage), and daily (air) emissions, indicating that the environmental levels were not significantly altered 8 years after co-processing RFD. The current levels of metals and PCDD/Fs in soil, vegetation and air found near the cement plant of Alcanar were in the low part of the range found in other similar areas of Catalonia. In all cases, the HQs due to exposure to trace elements and PCDD/Fs were lower than the safety value, which is defined as the unity ($HQ < 1$). In turn, carcinogenic risks were below the national 10^{-5} threshold. The present results corroborate that, from an environmental point of view, the use of wastes as AFs in cement plants operating with suitable technical conditions is a good solution for waste management, which enables abating the effect on climate change and fossil fuel depletion, while utilizing principles of circular economy.

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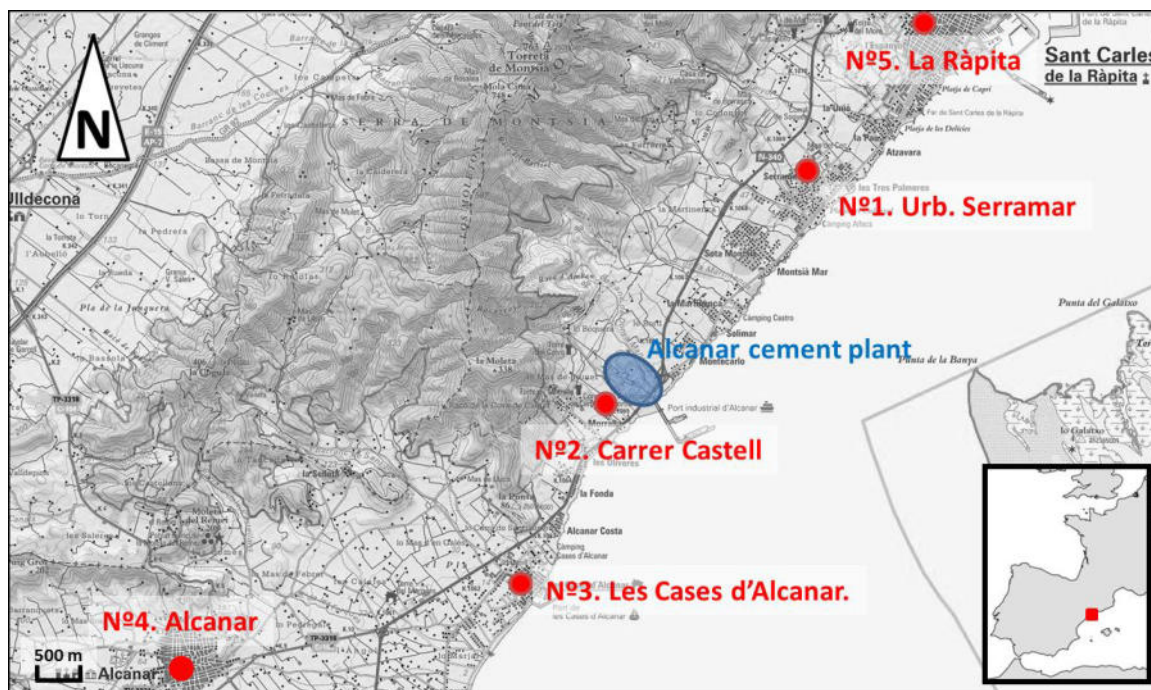
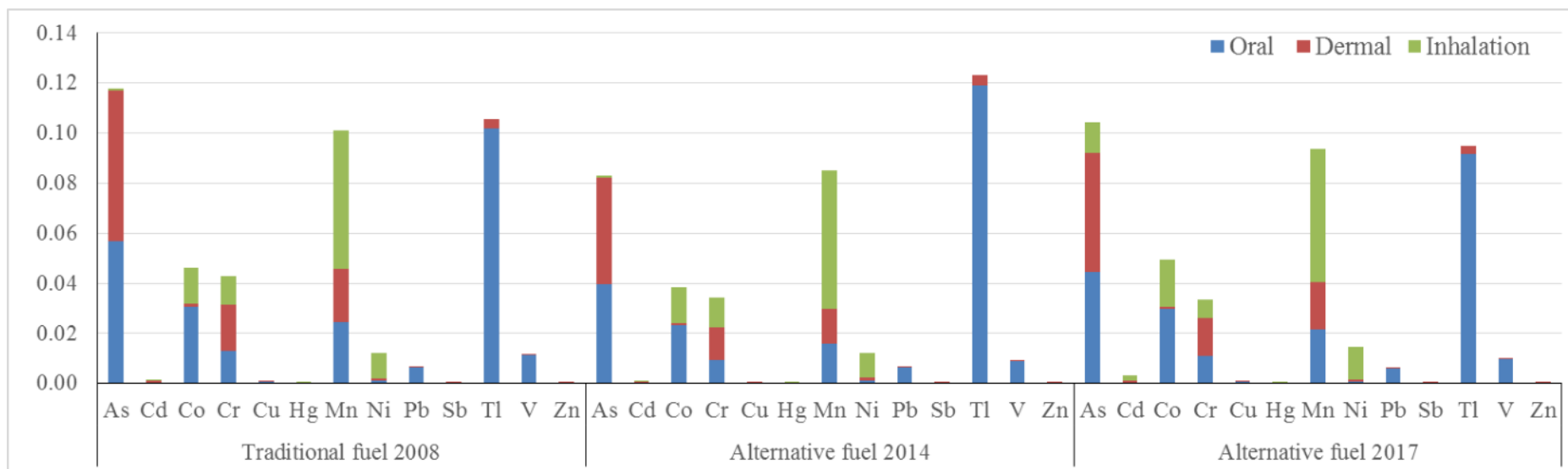


Figure 1. Sampling points of soil, herbage and air around the cement plant of Alcanar (Catalonia, Spain).



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435 **Figure 2.** Hazard quotient (unitless) derived from exposure to metals and PCDD/Fs for the population living in the vicinity of the Alcanar
 436 cement plant.

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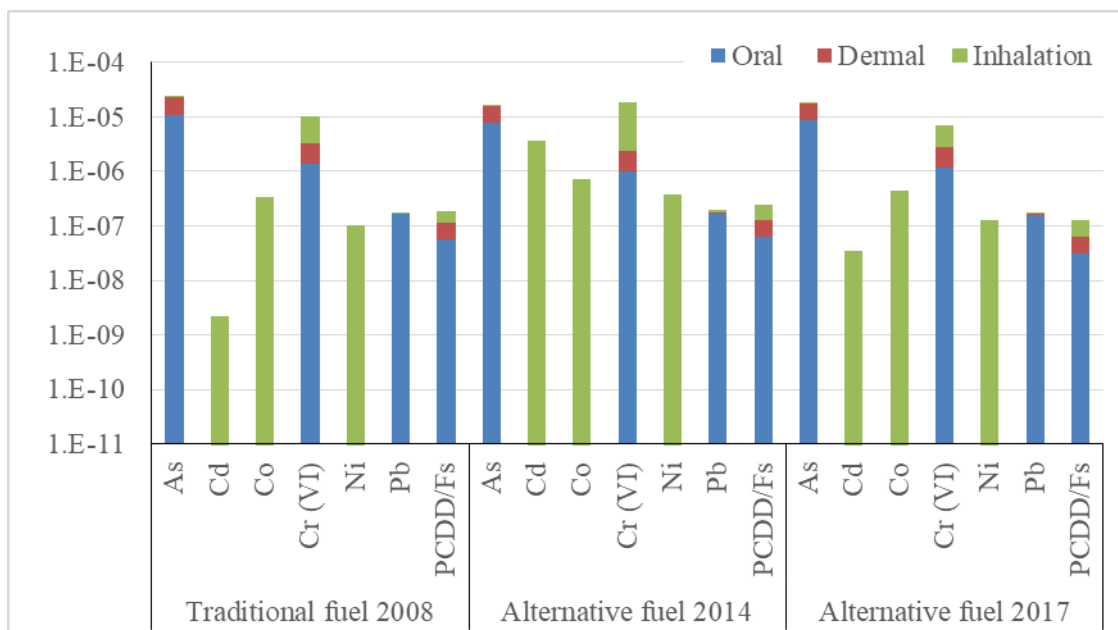


Figure 3. Carcinogenic risks (unitless) derived from exposure to metals and PCDD/Fs for the population living in the vicinity of the Alcanar cement plant.

Table 1. Concentrations of metals ($\mu\text{g/g}$) and PCDD/Fs (ng/kg) in soil samples collected around the cement plant of Alcanar (Catalonia, Spain) before (2008) and after (2014 and 2017) the partial substitution of fossil fuel by RDF.

	Traditional fuel	Alternative fuel		Temporal Variation (%)	
	2008	2014	2017		
	N=5	N=5	N=5	08-17	14-17
As	10.9 ± 2.88	7.65 ± 3.31	8.55 ± 5.76	-21	12
Cd	0.25 ± 0.07	0.23 ± 0.07	0.24 ± 0.11	-1	3
Co	5.91 ± 1.63	4.46 ± 1.45	5.71 ± 2.74	-3	28
Cr	24.8 ± 6.68	17.9 ± 5.42	20.7 ± 11.0	-17	16
Cu	15.6 ± 6.52	12.6 ± 4.23	23.3 ± 20.1	49	85
Hg	<0.10		0.05 ± 0.02		
Mn	$373^a \pm 105$	$242^b \pm 52.7$	$329^{ab} \pm 147$	-12	36
Ni	14.2 ± 3.38	15.2 ± 1.71	11.5 ± 6.42	-19	-24
Pb	28.8 ± 11.3	29.8 ± 15.8	27.9 ± 15.3	-3	-6
Sb	0.08 ± 0.06	0.08 ± 0.04	0.11 ± 0.09	44	44
Tl	0.65 ± 0.73	0.76 ± 0.93	0.59 ± 0.76	-10	-23
V	35.8 ± 8.92	28.7 ± 5.06	31.2 ± 17.0	-13	9
Zn	66.2 ± 37.3	49.9 ± 22.4	76.6 ± 21.4	16	53
2,3,7,8-TCDD	0.05 ± 0.04	0.03 ± 0.02	0.03 ± 0.02	-44	-6
1,2,3,7,8-PeCDD	0.10 ± 0.06	0.10 ± 0.08	0.08 ± 0.05	-25	-24
1,2,3,4,7,8-HxCDD	0.15 ± 0.14	0.15 ± 0.11	0.13 ± 0.09	-16	-17
1,2,3,6,7,8-HxCDD	0.34 ± 0.35	0.30 ± 0.13	0.21 ± 0.16	-37	-28
1,2,3,7,8,9-HxCDD	$0.27^{ab} \pm 0.25$	$0.38^a \pm 0.08$	$0.15^b \pm 0.10$	-46	-61
1,2,3,4,6,7,8-OCDD	7.00 ± 10.3	5.68 ± 3.70	5.48 ± 7.91	-22	-3
2,3,7,8-TCDF	53.5 ± 79.0	46.8 ± 41.5	37.4 ± 53.8	-30	-20
1,2,3,7,8-PeCDF	0.22 ± 0.13	0.18 ± 0.08	<0.25	-	-
2,3,4,7,8-PeCDF	$0.27^a \pm 0.26$	$0.21^{ab} \pm 0.10$	$0.11^b \pm .06$	-60	-49
2,3,4,7,8-PeCDF	0.23 ± 0.12	0.38 ± 0.29	0.15 ± 0.10	-33	-59
1,2,3,4,7,8-HxCDF	$0.30^{ab} \pm .021$	$0.64^a \pm 0.54$	$0.19^b \pm 0.13$	-38	-71
1,2,3,6,7,8-HxCDF	0.23 ± 0.16	$0.50^a \pm 0.40$	0.18 ± 0.13	-21	-63
1,2,3,7,8,9-HxCDF	<0.09	0.14 ± 0.15	< 0.08	-	-
2,3,4,6,7,8-HxCDF	0.36 ± 0.27	0.66 ± 0.64	0.21 ± 0.16	-41	-68
1,2,3,4,6,7,8-OCDF	$5.97^{ab} \pm 11.5$	$9.67^a \pm 16.5$	$0.99^b \pm 0.73$	-83	-90
1,2,3,4,7,8,9-OCDF	0.20 ± 0.14	0.54 ± 0.67	0.16 ± 0.11	-19	-70
ng WHO TEQ/kg	4.97 ± 8.07	6.60 ± 8.22	1.23 ± 0.93	-75	-81
	0.57 ± 0.50	0.72 ± 0.54	0.36 ± 0.22	-38	-50

^{a, b} Significant differences at $p < 0.05$).

Table 2. Concentrations of metals ($\mu\text{g/g}$) and PCDD/Fs (ng/kg) in herbage samples collected around the cement plant of Alcanar (Catalonia, Spain) before (2008) and after

	Traditional fuel		Alternative fuel		Temporal Variation (%)	
	2008		2014		2017	
	N=5	N=5	N=5	N=5	N=5	N=5
As	0.10 ± 0.08	0.06 ± 0.03	0.03 ± 0.02	-68	-49	
Cd	0.08 ± 0.10	0.02 ± 0.01	0.02 ± 0.01	-80	-2	
Co	$0.52^a \pm 0.03$	$0.09^b \pm 0.05$	$0.04^c \pm 0.02$	-93	-58	
Cr	$3.23^a \pm 1.07$	$1.52^b \pm 0.30$	$0.46^c \pm 0.37$	-86	-70	
Cu	$6.38^a \pm 1.95$	$4.51^b \pm 0.70$	$3.98^b \pm 0.73$	-38	-12	
Hg			0.01 ± 0.01	-	-	
Mn	$41.3^a \pm 6.10$	$31.81^b \pm 7.70$	$22.3^c \pm 5.48$	-46	-30	
Ni	$2.00^a \pm 0.66$	$1.20^b \pm 0.33$	$0.55^c \pm 0.24$	-72	-54	
Pb	$0.62^a \pm 0.39$	$0.21^b \pm 0.17$	$0.40^{ab} \pm 0.10$	-35	95	
Sb	0.06 ± 0.02	-		-100	-	
Tl	$0.02^a \pm 0.01$	$0.17^{ab} \pm 0.33$	$0.10^b \pm 0.08$	537	-43	
V	-	0.29 ± 0.18	0.17 ± 0.04	-	-41	
Zn	$36.2^a \pm 20.6$	$15.65^b \pm 1.47$	$23.00^a \pm 4.46$	-36	47	
2,3,7,8-TCDD	0.01 ± 0.01	0.02 ± 0.01	<0.02	-20		
1,2,3,7,8-PeCDD	<0.03	0.02 ± 0.01	<0.03			
1,2,3,4,7,8-HxCDD	0.01 ± 0.01	<0.03	0.02 ± 0.01	102		
1,2,3,6,7,8-HxCDD	0.02 ± 0.01	<0.03	0.03 ± 0.02	45		
1,2,3,7,8,9-HxCDD	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.03	38	31	
1,2,3,4,6,7,8-HpCDD	0.17 ± 0.06	0.10 ± 0.07	0.20 ± 0.24	16	101	
OCDD	$0.95^a \pm 0.28$	$0.38^b \pm 0.18$	$0.80^{ab} \pm 0.99$	-16	109	
2,3,7,8-TCDF	$0.06^a \pm 0.03$	$0.51^b \pm 0.32$	$0.13^{ab} \pm 0.15$	124	-74	
1,2,3,7,8-PeCDF	0.04 ± 0.02	0.22 ± 0.16	0.09 ± 0.09	133	-58	
2,3,4,7,8-PeCDF	0.05 ± 0.03	0.12 ± 0.08	0.07 ± 0.07	36	-45	
1,2,3,4,7,8-HxCDF	$0.04^a \pm 0.01$	$0.12^b \pm 0.06$	$0.08^{ab} \pm 0.09$	98	-32	
1,2,3,6,7,8-HxCDF	0.04 ± 0.01	0.04 ± 0.03	0.04 ± 0.06	6	1	
1,2,3,7,8,9-HxCDF	<0.03	<0.03	<0.03			
2,3,4,6,7,8-HxCDF	0.04 ± 0.03	0.03 ± 0.01	0.03 ± 0.03	-14	28	
1,2,3,4,6,7,8-HpCDF	$0.14^a \pm 0.04$	$0.49^b \pm 0.21$	$0.34^{ab} \pm 0.49$	144	-30	
1,2,3,4,7,8,9-HpCDF	<0.05	0.10 ± 0.07	<0.06		-70	
OCDF	$0.10^a \pm 0.05$	$0.43^b \pm 0.13$	$0.22^{ab} \pm 0.24$	116	-50	
ng WHO TEQ/kg	0.09 ± 0.02	0.16 ± 0.07	0.09 ± 0.06	0	-45	

(2014 and 2017) the partial substitution of fossil fuel by RDF.

^{a, b} Significant differences at $p < 0.05$.

Table 3. Concentrations of metals (ng/m³) and PCDD/Fs (pg/m³) in air samples collected around the cement plant of Alcanar (Catalonia, Spain) before (2008) and after (2014 and 2017) the partial substitution of fossil fuel by RDF.

	Traditional fuel	Alternative fuel		Temporal Variation (%)	
	2008	2014	2017		
	N=4	N=5	N=5	08-17	14-17
As	<0.02	0.24 ± 0.17	0.19 ± 0.11		-19
Cd	<0.01	<0.01	0.05 ± 0.01		
Co	0.09 ^{ab} ± 0.10	0.20 ^b ± 0.10	0.12 ^b ± 0.03	30	-41

Cr	1.23 ^{ab} ± 2.40	2.82 ^a ± 2.52	0.76 ^b ± 0.11	-38	-73
Cu	15.0 ± 14.6	32.03 ± 31.6	45.59 ± 28.07	204	42
Hg	<0.02	<0.02	<0.02		
Mn	2.89 ± 2.87	5.10 ± 3.32	2.78 ± 0.66	-4	-45
Ni	0.95 ^a ± 0.89	3.47 ^b ± 0.43	1.23 ^a ± 0.65	29	-65
Pb	0.49 ^a ± 0.60	3.57 ^b ± 2.57	1.86 ^{ab} ± 0.95	276	-48
Sb	<0.02	0.56 ± 0.36	0.26 ± 0.11	2491	-54
Tl	<0.01	0.29 ± 0.29	0.23 ± 0.23		-21
V	1.50 ^a ± 2.30	7.28 ^b ± 2.67	1.75 ^a ± 1.49	16	-76
Zn	NA	15.08 ± 9.22	11.23 ± 2.14	-	-26
2,3,7,8-TCDD	<0.001	0.001 ± 0.001	0.001 ± 0.000	-	0
1,2,3,7,8-PeCDD	0.001 ± 0.000	0.002 ± 0.004	0.001 ± 0.000	0	-50
1,2,3,4,7,8-HxCDD	0.001 ± 0.000	0.002 ± 0.003	0.001 ± 0.000	0	-50
1,2,3,6,7,8-HxCDD	0.001 ± 0.002	0.002 ± 0.004	0.001 ± 0.000	-50	-50
1,2,3,7,8,9-HxCDD	0.002 ± 0.001	0.003 ± 0.005	0.001 ± 0.000	-50	-67
1,2,3,4,6,7,8-HpCDD	0.013 ^a ± 0.012	0.012 ^{ab} ± 0.018	0.006 ^b ± 0.002	-54	-50
OCDD	0.029 ± 0.026	0.024 ± 0.021	0.021 ± 0.009	-28	-13
2,3,7,8-TCDF	0.002 ± 0.001	0.004 ± 0.006	0.004 ± 0.005	100	0
1,2,3,7,8-PeCDF	0.001 ± 0.001	0.003 ± 0.006	0.001 ± 0.000	0	-67
2,3,4,7,8-PeCDF	0.004 ^a ± 0.003	0.006 ^b ± 0.009	0.002 ^b ± 0.002	-50	-67
1,2,3,4,7,8-HxCDF	0.003 ± 0.001	0.005 ± 0.006	0.007 ± 0.005	133	40
1,2,3,6,7,8-HxCDF	0.004 ± 0.001	0.005 ± 0.005	0.002 ± 0.001	-50	-60
1,2,3,7,8,9-HxCDF	0.001 ^a ± 0.001	0.001 ^b ± 0.001	0.001 ^b ± 0.001	0	0
2,3,4,6,7,8-HxCDF	0.007 ^a ± 0.001	0.004 ^b ± 0.006	0.002 ^b ± 0.001	-71	-50
1,2,3,4,6,7,8-HpCDF	0.013 ^{ab} ± 0.007	0.044 ^a ± 0.0022	0.011 ^b ± 0.002	-15	-75
1,2,3,4,7,8,9-HpCDF	<0.007	<0.009	<0.009	-	-
OCDF	0.012	<0.034	<0.034	-	-
pg WHO TEQ/m ³	0.005 ± 0.002	0.008 ± 0.011	0.004 ± 0.001	-20	-50

^{a, b} Significant differences at p<0.05.

Table 4. Exposure to metals (mg/kg day) and PCDD/Fs (ng WHO-TEQ/kg·day) for the population living in the vicinity of the cement plant in Alcanar.

	Exposure route	Traditional fuel	Alternative fuel	
		2008	2014	2017
As	Soil Ingestion	$1.19 \cdot 10^{-5} \pm 5.16 \cdot 10^{-6}$	$1.19 \cdot 10^{-5} \pm 5.16 \cdot 10^{-6}$	$1.34 \cdot 10^{-5} \pm 8.99 \cdot 10^{-6}$
	Dermal Contact	$1.27 \cdot 10^{-5} \pm 5.50 \cdot 10^{-6}$	$1.27 \cdot 10^{-5} \pm 5.50 \cdot 10^{-6}$	$1.42 \cdot 10^{-5} \pm 9.58 \cdot 10^{-6}$
	Air Inhalation	NC	$6.46 \cdot 10^{-8} \pm 4.74 \cdot 10^{-8}$	$5.24 \cdot 10^{-8} \pm 2.90 \cdot 10^{-8}$
Cd	Soil Ingestion	$3.67 \cdot 10^{-7} \pm 1.07 \cdot 10^{-7}$	$3.67 \cdot 10^{-7} \pm 1.07 \cdot 10^{-7}$	$3.80 \cdot 10^{-7} \pm 1.79 \cdot 10^{-7}$
	Dermal Contact	$1.30 \cdot 10^{-8} \pm 3.79 \cdot 10^{-9}$	$1.30 \cdot 10^{-8} \pm 3.79 \cdot 10^{-9}$	$1.35 \cdot 10^{-8} \pm 6.37 \cdot 10^{-9}$
	Air Inhalation	NC	NC	$1.31 \cdot 10^{-8} \pm 2.67 \cdot 10^{-9}$
Co	Soil Ingestion	$6.97 \cdot 10^{-6} \pm 2.27 \cdot 10^{-6}$	$6.97 \cdot 10^{-6} \pm 2.27 \cdot 10^{-6}$	$8.91 \cdot 10^{-6} \pm 4.28 \cdot 10^{-6}$
	Dermal Contact	$2.48 \cdot 10^{-7} \pm 8.07 \cdot 10^{-8}$	$2.48 \cdot 10^{-7} \pm 8.07 \cdot 10^{-8}$	$3.17 \cdot 10^{-7} \pm 1.52 \cdot 10^{-7}$
	Air Inhalation	$5.47 \cdot 10^{-8} \pm 2.88 \cdot 10^{-8}$	$5.47 \cdot 10^{-8} \pm 2.88 \cdot 10^{-8}$	$3.22 \cdot 10^{-8} \pm 9.43 \cdot 10^{-9}$
Cr	Soil Ingestion	$2.79 \cdot 10^{-5} \pm 8.46 \cdot 10^{-6}$	$2.79 \cdot 10^{-5} \pm 8.46 \cdot 10^{-6}$	$3.23 \cdot 10^{-5} \pm 1.72 \cdot 10^{-5}$
	Dermal Contact	$9.91 \cdot 10^{-7} \pm 3.01 \cdot 10^{-7}$	$9.91 \cdot 10^{-7} \pm 3.01 \cdot 10^{-7}$	$1.15 \cdot 10^{-6} \pm 6.11 \cdot 10^{-7}$
	Air Inhalation	$7.73 \cdot 10^{-7} \pm 6.90 \cdot 10^{-7}$	$7.73 \cdot 10^{-7} \pm 6.90 \cdot 10^{-7}$	$2.08 \cdot 10^{-7} \pm 2.99 \cdot 10^{-8}$
Cu	Soil Ingestion	$1.96 \cdot 10^{-5} \pm 6.61 \cdot 10^{-6}$	$1.96 \cdot 10^{-5} \pm 6.61 \cdot 10^{-6}$	$3.64 \cdot 10^{-5} \pm 3.14 \cdot 10^{-5}$
	Dermal Contact	$6.97 \cdot 10^{-7} \pm 2.35 \cdot 10^{-7}$	$6.97 \cdot 10^{-7} \pm 2.35 \cdot 10^{-7}$	$1.29 \cdot 10^{-6} \pm 1.12 \cdot 10^{-6}$
	Air Inhalation	$8.78 \cdot 10^{-6} \pm 8.66 \cdot 10^{-6}$	$8.78 \cdot 10^{-6} \pm 8.66 \cdot 10^{-6}$	$1.25 \cdot 10^{-5} \pm 7.69 \cdot 10^{-6}$
Hg	Soil Ingestion	NC	NC	$7.81 \cdot 10^{-8} \pm 3.40 \cdot 10^{-8}$
	Dermal Contact	NC	NC	$2.77 \cdot 10^{-9} \pm 1.21 \cdot 10^{-9}$
	Air Inhalation	NC	NC	NC
Mn	Soil Ingestion	$3.78 \cdot 10^{-4} \pm 8.23 \cdot 10^{-5}$	$3.78 \cdot 10^{-4} \pm 8.23 \cdot 10^{-5}$	$5.14 \cdot 10^{-4} \pm 2.29 \cdot 10^{-4}$
	Dermal Contact	$1.34 \cdot 10^{-5} \pm 2.93 \cdot 10^{-6}$	$1.34 \cdot 10^{-5} \pm 2.93 \cdot 10^{-6}$	$1.83 \cdot 10^{-5} \pm 8.15 \cdot 10^{-6}$
	Air Inhalation	$1.40 \cdot 10^{-6} \pm 9.11 \cdot 10^{-7}$	$1.40 \cdot 10^{-6} \pm 9.11 \cdot 10^{-7}$	$7.63 \cdot 10^{-7} \pm 1.80 \cdot 10^{-7}$
Ni	Soil Ingestion	$2.38 \cdot 10^{-5} \pm 2.67 \cdot 10^{-6}$	$2.38 \cdot 10^{-5} \pm 2.67 \cdot 10^{-6}$	$1.80 \cdot 10^{-5} \pm 1.00 \cdot 10^{-5}$
	Dermal Contact	$8.46 \cdot 10^{-7} \pm 9.47 \cdot 10^{-8}$	$8.46 \cdot 10^{-7} \pm 9.47 \cdot 10^{-8}$	$6.40 \cdot 10^{-7} \pm 3.56 \cdot 10^{-7}$
	Air Inhalation	$9.50 \cdot 10^{-7} \pm 1.17 \cdot 10^{-7}$	$9.50 \cdot 10^{-7} \pm 1.17 \cdot 10^{-7}$	$3.36 \cdot 10^{-7} \pm 1.79 \cdot 10^{-7}$
Pb	Soil Ingestion	$4.65 \cdot 10^{-5} \pm 2.46 \cdot 10^{-5}$	$4.65 \cdot 10^{-5} \pm 2.46 \cdot 10^{-5}$	$4.36 \cdot 10^{-5} \pm 2.39 \cdot 10^{-5}$
	Dermal Contact	$1.65 \cdot 10^{-6} \pm 8.74 \cdot 10^{-7}$	$1.65 \cdot 10^{-6} \pm 8.74 \cdot 10^{-7}$	$1.55 \cdot 10^{-6} \pm 8.47 \cdot 10^{-7}$
	Air Inhalation	$9.79 \cdot 10^{-7} \pm 7.04 \cdot 10^{-7}$	$9.79 \cdot 10^{-7} \pm 7.04 \cdot 10^{-7}$	$5.08 \cdot 10^{-7} \pm 2.59 \cdot 10^{-7}$
Sb	Soil Ingestion	$1.19 \cdot 10^{-7} \pm 5.71 \cdot 10^{-8}$	$1.19 \cdot 10^{-7} \pm 5.71 \cdot 10^{-8}$	$1.72 \cdot 10^{-7} \pm 1.37 \cdot 10^{-7}$
	Dermal Contact	$4.23 \cdot 10^{-9} \pm 2.03 \cdot 10^{-9}$	$4.23 \cdot 10^{-9} \pm 2.03 \cdot 10^{-9}$	$6.10 \cdot 10^{-9} \pm 4.87 \cdot 10^{-9}$
	Air Inhalation	NC	$1.54 \cdot 10^{-7} \pm 9.91 \cdot 10^{-8}$	$7.10 \cdot 10^{-8} \pm 2.92 \cdot 10^{-8}$
Tl	Soil Ingestion	$1.19 \cdot 10^{-6} \pm 1.44 \cdot 10^{-6}$	$1.19 \cdot 10^{-6} \pm 1.44 \cdot 10^{-6}$	$9.16 \cdot 10^{-7} \pm 1.18 \cdot 10^{-6}$
	Dermal Contact	$4.23 \cdot 10^{-8} \pm 5.13 \cdot 10^{-8}$	$4.23 \cdot 10^{-8} \pm 5.13 \cdot 10^{-8}$	$3.25 \cdot 10^{-8} \pm 4.21 \cdot 10^{-8}$
	Air Inhalation	$7.82 \cdot 10^{-8} \pm 7.82 \cdot 10^{-8}$	$7.82 \cdot 10^{-8} \pm 7.82 \cdot 10^{-8}$	$6.20 \cdot 10^{-8} \pm 6.42 \cdot 10^{-8}$
V	Soil Ingestion	$4.48 \cdot 10^{-5} \pm 7.90 \cdot 10^{-6}$	$4.48 \cdot 10^{-5} \pm 7.90 \cdot 10^{-6}$	$4.88 \cdot 10^{-5} \pm 2.65 \cdot 10^{-5}$
	Dermal Contact	$1.59 \cdot 10^{-6} \pm 2.81 \cdot 10^{-7}$	$1.59 \cdot 10^{-6} \pm 2.81 \cdot 10^{-7}$	$1.73 \cdot 10^{-6} \pm 9.41 \cdot 10^{-7}$
	Air Inhalation	NC	$1.99 \cdot 10^{-6} \pm 7.30 \cdot 10^{-7}$	$4.79 \cdot 10^{-7} \pm 4.07 \cdot 10^{-7}$
Zn	Soil Ingestion	NC	$7.80 \cdot 10^{-5} \pm 3.50 \cdot 10^{-5}$	$1.20 \cdot 10^{-4} \pm 3.35 \cdot 10^{-5}$
	Dermal Contact	NC	$2.77 \cdot 10^{-6} \pm 1.24 \cdot 10^{-6}$	$4.25 \cdot 10^{-6} \pm 1.19 \cdot 10^{-6}$
	Air Inhalation	$4.78 \cdot 10^{-6} \pm 2.53 \cdot 10^{-6}$	$4.78 \cdot 10^{-6} \pm 2.53 \cdot 10^{-6}$	$3.23 \cdot 10^{-6} \pm 5.85 \cdot 10^{-7}$
PCDD/Fs	Soil Ingestion	$1.02 \cdot 10^{-6} \pm 8.95 \cdot 10^{-7}$	$1.12 \cdot 10^{-6} \pm 8.44 \cdot 10^{-7}$	$5.55 \cdot 10^{-7} \pm 3.44 \cdot 10^{-7}$
	Dermal Contact	$1.09 \cdot 10^{-6} \pm 5.93 \cdot 10^{-7}$	$1.19 \cdot 10^{-6} \pm 8.99 \cdot 10^{-7}$	$5.92 \cdot 10^{-7} \pm 3.67 \cdot 10^{-7}$
	Air Inhalation	$1.30 \cdot 10^{-6} \pm 4.46 \cdot 10^{-7}$	$2.13 \cdot 10^{-6} \pm 3.01 \cdot 10^{-6}$	$1.14 \cdot 10^{-6} \pm 2.73 \cdot 10^{-7}$

3

4 NC: Not calculated.